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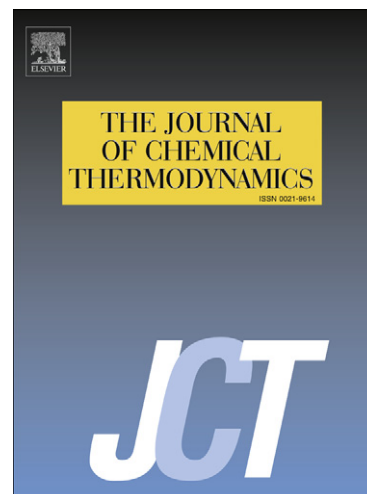
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**Density, conductivity, viscosity, and excess properties of (pyrrolidinium
nitrate-based Protic Ionic Liquid + propylene carbonate) binary mixture**

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Abstract

Density, ρ , viscosity, η , and conductivity, σ , measurements of binary mixtures containing the pyrrolidinium nitrate Protic Ionic Liquid (PIL) and propylene carbonate (PC), are determined at the atmospheric pressure as a function of the temperature from (283.15 to 353.15) K and within the whole composition range. The temperature dependence of both the viscosity and conductivity of each mixture exhibits a non-Arrhenius behaviour, but is correctly fitted by using the Vogel-Tamman-Fulcher (VTF) equation. In each case, the best-fit parameters, such as the pseudo activation energy, E_a^* and ideal glass transition temperature, T_0 are then extracted. The excess molar volumes V^E , and viscosity deviations from the ideality, $\Delta\eta$, of each investigated mixture were then deduced from the experimental results, as well as, their apparent molar volumes, V_ϕ , thermal expansion coefficients α_p , and excess Gibbs energies (ΔG^{*E}) of activation of viscous flow. The V^E , α_p^E , $\Delta\eta$ values are negative over the whole composition range for each studied temperature therein. According to the Walden rule, the ionicity of each mixture was then evaluated as a function of the temperature from (283.15 to 353.15) K and of the composition. Results have been then discussed in terms of molecular interactions and molecular structures in this binary mixture.

Keywords: Protic ionic liquid, propylene carbonate, density, heat capacity, viscosity, excess properties.

1. Introduction

Ionic liquids (ILs) are a class of chemicals composed entirely of ions having melting points below $T = 373$ K. Due to their unique physicochemical properties, ILs are rapidly gaining interest as greener replacements for traditional volatile organic solvents (VOCs). Other benefits are their large liquid temperature ranges driven by low melting temperatures and high decomposition temperatures, favourable solvation behaviour, high stability in air, high ionic conductivity, and modification of selectivity in chemical reactions, which open new possibilities in various industrial fields as catalysis, separation techniques, and electrochemical devices applications [1-13]. However, any industrial development requires reliable reference data on the thermodynamic properties of pure ILs and their mixtures with other solvents. In spite of extensive applications little information on their thermodynamic properties are published [14-23].

Most ILs are based on heterocyclic compounds, particularly the alkyimidazolium, alkylpyrrolidinium, or alkylpyridinium cations. They can be broadly classified into two groups, protic and aprotic ILs [24,25]. Protic ionic liquids (PILs) are synthesized by proton transfer from a Brønsted acid to a Brønsted base, which creates proton donor and acceptor sites and can lead to the formation of hydrogen bonds [25]. The research concerning PILs has generally focused on surfactant self-assembly [26–32], and their physical properties [23,24,33–34]. Due to their excellent catalytic effects and other advantages such as easy preparation, cheap cost, and low toxicity, their physicochemical properties have also attracted researcher's attention [35-38]. For example, recently, Nakamoto *et al.* have reported that PILs are processing candidates as electrolyte for electrochemical storage and conversion devices [39,40]. Indeed, our group has recently shown that the labile proton on PILs structure participates to the pseudo capacitance on

the fast redox reactions at the electrode/electrolyte interface in the case of activated carbon-based super capacitors.[41,42] However, despite the exceptional properties of these promising electrolytes, very few study concerning the physical properties of pure PILs as well as their mixtures with classical solvents for batteries or super capacitors has been reported in the literature. Previously, our group has presented a series of thermodynamic properties (such as specific heat capacities, volumetric and, rheological properties) for different PILs in mixtures with molecular solvents, such as acetonitrile, water, and alcohols [43,44]. Nevertheless, classical batteries electrolytes are generally composed of salt (*e.g.* lithium salt or an IL) dissolved in an alkylcarbonate solvents mixture. To the best of our knowledge, no thermodynamic data of electrolyte based on an alkylcarbonate mixed with any PIL is, up-to date, available in the literature.

Herein, we report a thermodynamic study of pyrrolidinium nitrate-based PIL, [Pyr][NO₃], in mixture with the propylene carbonate, PC. Their volumetric, thermal and transport properties are presented as the function of temperature and composition, and then discussed in order to understand the molecular interactions between (individual ion - PC), (cation - anion), and (PILs ions pair - PC) in solution. Finally, all thermodynamics properties of the ([Pyr][NO₃] + PC) binary mixture presented in this paper are then compared with those already reported by our group in the case of the ([Pyr][NO₃] + water) mixture [43].

2. Experimental

2.1. Materials

Nitric acid solution (68 % in water), pyrrolidine, propylene carbonate (PC) and 1,2-dichloroethane, (DCE), used in this study are commercially available from Fluka within a molecular purity > 99 % and were used without further purification. Pyrrolidinium nitrate was prepared according to the methodology previously described by our group [45]. Briefly, the amine was placed in a triple necked flask equipped with a reflux condenser; nitric acid was added drop wise to the flask stirring with a magnetic bar. After reaction, 120 cm³ of DCE was then added to obtained aqueous solution. Subsequently, in order to remove the water, the mixture was distilled under normal pressure until the water–DCE hetero-azeotropic boiling point temperature was reached (*e.g.* 346.15 K). DCE was then evaporated from the mixture under reduced pressure enabling a pale yellow and viscous liquid to be collected within a yield close to 93-98 %. Finally pyrrolidinium nitrate was dried overnight at $T = 343$ K under high vacuum (0.1 Pa) prior to use. Solid pale yellow crystals, containing less than 100×10^{-6} of residual water measured by using a Coulometric Karl-Fischer titrator, were then obtained, and stored at ambient temperature for a few weeks. It should be important to notify that this PIL is then liquid within a water content close to 2000×10^{-6} . Since pure PIL with this residual quantity of water was used during each measurement reported herein, such purity state was defined into this paper as the pure PIL. The water content in PC was quantified as below 10×10^{-6} . Information (*i.e.* source, abbreviation, purity, and water content) for each chemical sample studied in this paper are summarized in table 1.

2.2. Methods

Binary mixtures containing pyrrolidinium nitrate, [Pyr][NO₃], and propylene carbonate, PC, were prepared by mass with an accuracy of $\pm 1 \times 10^{-4}$ g using a Sartorius 1602 MP balance.

The density of the pure components and their mixtures was determined by using an Anton Parr digital vibrating tube densitometer (model 60/602, Anton Parr, France) from (283.15 to 353.15) K. The densitometer was firstly calibrated at all temperatures with degassed water and dehumidified air at atmospheric pressure as recommended by the constructor. More than five readings were taken for each density measurement reported therein. The uncertainty of the density, and of excess volume values were better than 5×10^{-5} g·cm⁻³ and 0.007 cm³·mol⁻¹, respectively.

A TA Instruments rheometer AR 1000 was used to determine the rheological behaviour and the viscosity (η) of the pure [Pyr][NO₃] by using a conical geometry. The temperature in the cell was regulated within ± 0.01 K with a solid-state thermostat. After ensuring that the studied ionic liquid presented a Newtonian behaviour, rheograms were recorded at atmospheric pressure as a function of temperature from (283.15 to 353.15) K for the pure [Pyr][NO₃], as well as, their mixtures with PC, within an operating speed of 50 rad·s⁻¹. The viscosity standard (Brookfield, 12700 mPa·s at 25 °C) and water were used to calibrate the rheometer. From this study, the uncertainty of viscosity measurements did not exceed ± 1 %.

Conductivity measurements were performed by using a Crison GLP31 digital multi-frequencies conductometer between (1000 and 5000) Hz. The temperature control from (258.15 to 363.15) K

is ensured within ± 0.01 K by means of a JULABO thermostatted bath. The conductometer was first calibrated with standard solutions of known conductivity (*i.e.* (0.1 and 0.02) mol·dm⁻³ KCl aqueous solutions), the uncertainty of reported conductivities did not exceed ± 2 %. The conductivity measurements of the ([Pyrr][NO₃] + PC) solutions were carried-out by continuous addition of pure [Pyrr][NO₃] into PC. Each conductivity was recorded when its stability was better than 1 % within 2 min.

3. Results and discussion

3.1. Effect of propylene carbonate on volumetric properties of the pyrrolidinium nitrate

3.1.1. Density data and excess molar volumes

The density of pure components and of ([Pyrr][NO₃] + PC) mixtures was measured as a function of the temperature from (283.15 to 353.15) K and the results are listed herein in table 2, shown in figure 1 and in figure S1 providing supporting information. From these as expected, it can be seen that the density decreases linearly with temperature and increases with the mole fraction of PIL in the binary mixture. In other words, the [Pyrr][NO₃] is denser than the PC (and its mixture with PC) over the whole temperature range studied. For example, the density values of pure PC and [Pyrr][NO₃] are close to (1.263 and 1.2350) g·cm⁻³ and to (1.1416 and 1.1820) g·cm⁻³ at $T =$ (283.15 and 353.15) K, respectively. The density data were then fitted by using a linear relationship as a function of temperature and by using a cubic polynomial function as a function of the composition. Each individual parameter of both fitting processes are reported in the Tables S1 and S2 providing on the supporting information along with their calculated standard deviations.

Excess molar volumes, V^E were then calculated from density measurements according to the following equation:

$$V^E = \left[\frac{(x_1 M_1 + x_2 M_2)}{\rho} \right] - \left[\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right] = V_m - \left[\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right] \quad (1)$$

where x_i , M_i , ρ_i are, respectively, the mole fraction, the molar mass, and the density of component i ; ρ and V_m are the experimental density (see table 2) and molar volume (see table S3 on the supporting information) of the binary mixture.

The experimental V^E results for the ([Pyrr][NO₃] + PC) binary mixture as a function of PIL composition, x_{PIL} , and of temperature from (283.15 to 353.15) K are presented in table 2 and figure 2. It can be observed from the experimental results that, the excess molar volumes V^E are negative over the entire composition and temperature ranges studied therein. Furthermore, V^E becomes more negative by increasing the temperature. For example, by increasing the temperature from (283.15 to 353.15) K, V^E maxima were shifted from $x_{\text{PIL}} = 0.40$ to $x_{\text{PIL}} = 0.50$, within values close (-0.3 and to -0.9) cm³·mol⁻¹, respectively.

Generally, the specific interactions in the mixture, typically H-bonds, break up as the temperature increases, while the dependence on temperature of the non-specific interactions is lighter and can usually be neglected [46]. By increasing the temperature, the PIL structure becomes less ordered, in the case of the ([Pyrr][NO₃] + PC) binary mixture, this structure change provides the more labile proton a freer and greater possibility to establish hydrogen bonds with the polar but non-associative carbonyl group on PC structure. This structure change induces then an increase of interaction between ions in solution and PC, and thus of volume contraction as a function of temperature as shown in figure 2 by comparing V^E values between (283.15 and 353.15) K. We also note that the concentration of labile proton accentuates this effect, this may explain the shift of the maximum to the high concentrations of PIL from $x_{\text{PIL}} = 0.40$ to $x_{\text{PIL}} = 0.50$. Comparatively, in the case of ([Pyrr][NO₃] + water) binary mixture, all V^E values are positive for temperature from (298.15 to 333.15) K over the whole composition range and

become more positive by increasing the temperature with a V^E maxima close to $x_{PIL} = 0.12$. In this later case, by increasing the temperature, H-bond break-up allows volume dilatation of the aqueous solution [43].

Based on the experimental density, the molar volume, V_m , of pure components and their mixtures could be also calculated in nm^3 by using the following equation:

$$V_m = \frac{(x_1 M_1 + x_2 M_2)}{N_a \cdot \rho} \quad (2)$$

where x_i and M_i are, respectively, the mole fraction, and the molar mass of component i ; N_a and ρ are the Avogadro's constant and the density of the binary mixture, respectively.

The values of molar volume, V_m , of pure components and their mixtures expressed in $\text{cm}^3 \cdot \text{mol}^{-1}$ and in nm^3 are reported in the table S3 providing on the supporting information.

In the case of the pure $[\text{Pyrr}][\text{NO}_3]$, by using $M_{PIL} = 134.13 \text{ g} \cdot \text{mol}^{-1}$, the calculated V_m value is close to 0.182 nm^3 at $T = 298.15 \text{ K}$. According to Glasser *et al.* [47], the standard entropy, S° , can be calculated within the prior knowledge of the molar volume of a component at $T = 298.15 \text{ K}$ by using the following simple expression:

$$S^\circ(298.15\text{K})/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 1246.5 \times (V_m/\text{nm}^3) + 29.5 \quad (3)$$

The value of the standard entropy calculated by equation 3 in the case of the pure $[\text{Pyrr}][\text{NO}_3]$ is $256.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, which is much lower, for example, than the value of $392.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ calculated in the case of the pure 1-ethyl-3-methylimidazolium lactate, $[\text{emim}][\text{L}]$ [48]. By

extending this methodology in the case of studied binary mixture compositions, the variation of excess standard entropy, S^E , at $T = 298.15$ K can be calculated as follows:

$$S^E = S_m^\circ - [x_1 S_1^\circ + x_2 S_2^\circ] \quad (4)$$

where x_i and S_i° are, respectively, the mole fraction and the standard entropy of component i .

The S_m° is the standard entropy of the binary mixture calculated by using equation 3 with molar volumes reported at $T = 298.15$ K in the table S3 in the supporting information.

Entropy values are reported at $T = 298.15$ K in the table S4 providing supporting information. It appears, as expected from equation 3 and from the variation of the molar volume as a function of the PIL composition, that the standard entropy of mixtures, S_m° , increases from (205.6 to 256.3) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ with the variation of the PIL mole fraction from $x_{\text{PIL}} = (0 \text{ to } 1)$, respectively. Concerning the variation of the excess standard entropy, S^E , as a function of the PIL mole fraction, x_{PIL} , we observed first that all S^E values are negative, and these values reach a maximum at $x_{\text{PIL}} = 0.40$, as shown in figure S2 available in the supporting information. These observations can be then linked to the fact that the real disorder of the ([Pyrr][NO₃] + PC) is lower than that expected from the ideality rule, which can may be then linked to a volume contraction by adding PC in [Pyrr][NO₃]. Such observations are, in fact, in good agreement with the obtained variation of the excess molar volumes as a function of the PIL mole fraction, as observed in figure 2.

3.1.2. Apparent and partial molar volumes

The apparent molar volumes $V_{\phi,i}$ of a component in the binary mixture such as the ([Pyrr][NO₃] ($i=1$) + PC ($i=2$)) is defined as:

$$V_{\phi,1} = \frac{V_m - x_2 V_{m,2}}{x_1} \quad (5)$$

where V_m is the molar volume of the mixture, x_1 and x_2 are the mole fraction of components 1 and 2 in the binary mixture, respectively. The $V_{m,2}$ is the molar volume of the pure component 2.

The combination of equations 1 and 5 gives the following set of equations:

$$V_{\phi,1} = V_{m,1} + \frac{V^E}{x_1} \quad (6)$$

$$V_{\phi,2} = V_{m,2} + \frac{V^E}{x_2} \quad (7)$$

As shown in figure 3, $V_{\phi,1}$ and $V_{\phi,2}$ values, reported in table S5 of the Supporting Information, increase with the PIL mole fraction x_{PIL} and with the temperature. For the temperature range studied herein, at infinite dilution the apparent molar volumes of the pure components (PIL or PC), $V_{\phi,i}$, are both lesser than the molar volumes of the pure components, $V_{m,i}$. For example at $T = 283.15$ K, [Pyrr][NO₃] has a molar volume close to $108.61 \text{ cm}^3 \cdot \text{mol}^{-1}$, but an apparent molar volume at low PIL concentration lower than $106.94 \text{ cm}^3 \cdot \text{mol}^{-1}$. In other words, in the case of the ([Pyrr][NO₃] + PC) infinite dilution solutions, both molecules have lower volumes than those expected from their molecular volumes. This experimental observation is may be due to the presence of the strong interactions in solution between ions (cation and anion) and PC resulting to a decrease of the occupied volume by each component, as well as, a contraction of the molar volume of the solution (*e.g.* negative excess molar volumes).

The partial and excess partial molar volumes have frequently been used to give an insight on solute–solvent interactions. Therefore the partial molar volume of the PIL in the mixture has been calculated using the following relation:

$$\bar{V}_{m,1} = V_{m,1} + \frac{V^E}{x_1} + x_1(1 - x_1) \left[\frac{\partial(V^E/x_1)}{\partial x_1} \right] \quad (8)$$

where $\bar{V}_{m,1}$ and $V_{m,1}$ are the partial molar volume of the PIL in the solution and the molar volume of the pure PIL, respectively.

The variation of the partial molar volume of the components, $\bar{V}_{m,i}$, of the ([Pyrr][NO₃] + PC) binary mixture as a function of composition and temperature from (283.15 to 353.15) K, are reported in table S6 of the supporting information. Figure 4 shows the variation of the $\bar{V}_{m,i}$ for PC and for [Pyrr][NO₃] in the ([Pyrr][NO₃] + PC) binary system as a function of temperature and composition. From this information, infinite dilution values, \bar{V}_i^∞ , reported in table 3 were determined by graphical extrapolation of $\bar{V}_{m,i}$ to $x_i = 0$ for each temperature investigated.

The partial molar volumes of the components of a mixture vary with the composition of the mixture, because the environment of the molecules in the mixture changes with the composition. It is the changing molecular environment, and the consequent alteration of the interactions between molecules that results in change on the volume occupied by a given number of molecules. This change depends upon the identity of the surrounding molecules such as herein, PC, [Pyrr]⁺, [NO₃]⁻. The utility of the limiting apparent molar volume of electrolytes lies in the additivity principle *i.e.* $\bar{V}_{m,1}$ is equal to the sum of its ionic components. The intrinsic partial molar ionic volume can be approximated by the van der Waals volume, V_{vdW} , which is the

volume of the ion impenetrable to solvent molecules, the difference between the partial molar ionic volume and its van der Waals volume may be discussed by considering the sign of this difference for the ion. When this quantity is negative, the ion is classified as an electrostatic “positive solvating ion”, and when the quantity is positive, the ion can be classified as a “negative solvating ion”. According to this classification, [Pyrr][NO₃] are positive solvating ions. It seems reasonable to regard the investigated PIL as ions which disorganize the bulk PC structure while organizing a portion of the solvent through a strong [Pyrr]⁺ cations and PC attraction *viz.* H-bonds in solution. This effect compresses a portion of the PC and thus shrinks the system. The shrinking is much greater at high temperature than at low.

3.1.3. Thermal expansion

The coefficient of thermal expansion (CTE) at constant pressure and composition, α_p for ([Pyrr][NO₃] + PC) system was calculated from experimental density values as a function of temperature and composition according to the following equation:

$$\alpha_p = -\frac{(\partial\rho/\partial T)_{p,x}}{\rho} \quad (9)$$

Calculated α_p values of the ([Pyrr][NO₃] + PC) binary mixture are reported in table S7. From this information, it appears that the thermal expansion coefficients at each composition increase with the temperature. Furthermore, the thermal expansion coefficients of the ([Pyrr][NO₃] + PC) binary mixture decrease by increasing the PIL mole fraction. In other words, for each temperature studied, the thermal coefficient of pure [Pyrr][NO₃] is lower than that observed in pure PC. For example, α_p values of $(8.74 \text{ and } 9.31) \times 10^4 \text{ K}^{-1}$ and of $(6.14 \text{ and } 6.42) \times 10^4 \text{ K}^{-1}$ are obtained at $T = (283.15 \text{ and } 353.15) \text{ K}$ in the case of the pure PC and [Pyrr][NO₃], respectively.

Additionally, the variation of the excess thermal expansion coefficient of the ([Pyrr][NO₃] + PC) system as a function of the temperature and of the volume fraction ϕ_{PIL} was then investigated.

For that, the excess thermal expansion coefficient α_p^E has been then determined as follows:

$$\alpha_p^E = \alpha_p - (\phi_1 \alpha_{p,1} + \phi_2 \alpha_{p,2}) \quad (10)$$

where $\alpha_{p,1}$ and $\alpha_{p,2}$ are, respectively, the thermal expansion coefficient for pure components 1 and 2. The ϕ_1 and ϕ_2 are the volume fraction for pure components 1 and 2 in the mixture, respectively.

As shown in figure 5, the α_p^E deviation is negative over the whole composition and over the studied temperature range. Furthermore, α_p^E maxima are localized at $\phi_{\text{PIL}} = 0.5$, and slightly decrease with the temperature. Comparatively, in the case of ([Pyrr][NO₃] + water) binary mixture, the α_p^E deviation is positive over the whole composition and over the studied temperature range with an amplitude twice as large [43].

The magnitude of the CTE depends on the structure of the material. In any (IL + molecular solvent) solution, such as the ([Pyrr][NO₃] + PC) mixture, this magnitude, as well as the α_p^E deviation, can be explained by the increase of mobility of each component in this mixture (*e.g.* ions, and PC) with the temperature and composition, this change is mainly driven by the fluctuation of enthalpy (cross interaction) and entropy (reorganization of the liquid phase *via* the cavities) of pure liquids and their mixture. Positive values of α_p^E are generally due to self-association of components in the mixture, and the components of mixture are strongly associated in the pure state and in the mixture. In other words, α_p^E values may reflect the molecular orientation and packing of mixtures. Molecular orientation effects are ascribed to shapes of molecules for non-polar solvents and dipole moments, higher multipole moments, and special interactions such as hydrogen bonds for polar solvents. These special interactions are in fact

more important in the case of polar and associative solvent such as water than in the case of polar but non-associative solvent like the PC. We can then conclude that in ([Pyrr][NO₃] + PC) mixture, associations between [Pyrr][NO₃] and PC are lesser than those observed in the case of the ([Pyrr][NO₃] + water) solution between [Pyrr][NO₃] and water.

3.2. Effect of propylene carbonate on transport properties of the pyrrolidinium nitrate

3.2.1. Conductivity measurements of the ([Pyrr][NO₃] + PC) binary mixture as a function of temperature and composition

The conductivity of pure PIL and of ([Pyrr][NO₃] + PC) mixtures was measured as a function of the temperature from (258.15 to 363.15) K and are listed in table S8 of the supporting information and shown in figures 6 and 7.

As expected and shown in the Figure 6, the conductivity of each composition increases with the temperature [49]. For example, the conductivity of pure [Pyrr][NO₃] is close to (29.3 and to 104.8) mS·cm⁻¹ at $T = (284.15 \text{ and } 353.65) \text{ K}$, respectively.

For x_{PIL} higher than 0.7, the curve $\sigma = f(T)$ exhibits a sharp drop in conductivity at temperatures around 293 K, as exemplified in the insert plot reported in figure 6 in the case of the x_{PIL} equals to 0.8. Similar behaviour has been already observed in the case of the [emim]I by Ganapatibhotla *et al.*[50] These authors have then explained this observed sharp decrease on the conductivity as a function of the temperature and composition by different changes of states (crystallization/liquefaction) between the solid and the liquid phases of involved mixtures. Herein, we have also assumed that observed conductivity drops are mainly due to the crystallization/liquefaction of the ([Pyrr][NO₃] + PC) binary mixture at temperatures close to 293

K in the case of the ([Pyrr][NO₃] + PC) binary mixture within x_{PIL} higher than 0.7. The figure 7 shows the dependence of the conductivity on the PIL weight and mole fractions (see the insert graph in the figure 7 and data listed in table S9 in the supporting information) for selected mixtures at various temperatures. From which, it can be seen that the conductivity increases by increasing the amount of PIL in the mixture until to reach the specific conductivity of the neat PIL. From figure 7, it can be also observed that there is a break in the trend of conductivity as a function of the [Pyrr][NO₃] weight fraction composition, w_{PIL} between conductivity values of mixture highly concentrated salt solutions and of the pure PIL.

The temperature dependence on the conductivity, for both neat PIL and its mixtures with PC, as a function of temperature from (263.15 to 368.15) K does not obey to the Arrhenius' law, reported in the equation 11 and shown in figure S3 providing in the supporting information.

In the ([Pyrr][NO₃] + PC) mixture, the strong interaction between anion and cation is replaced by strong intermolecular interactions between [Pyrr]⁺ cation and PC *via* the hydrogen bonds. This trend can be explained by the high degree of organization in the mixture, as well as, in pure PIL.

$$\sigma = \sigma_0 \exp\left(\frac{-E_a^\sigma}{RT}\right) \quad (11)$$

where E_a^σ , σ_0 and R are the activation energy calculated by the Arrhenius law applied for the conductivity as a function of the temperature, the conductivity limit calculated at $T = 0$ K and the universal gas constant, respectively. Adjustable parameters are summarized in table S10 in the supporting information.

Nevertheless, the temperature dependence of each solution studied herein is correctly fitted by VTF equation reported into the equation 12 as shown in the figure 6.

$$\sigma = \sigma_0^* \exp\left(\frac{-B_\sigma}{T - T_0^\sigma}\right) \quad (12)$$

where B_σ , σ_0^* and T_0^σ are adjustable parameters reported in table S11 of the supporting information.

For binary mixtures containing PILs, the values of the pseudo activation energy, E_a^* , calculated from the B_σ coefficient as:

$$E_a^* = B_\sigma \times R \quad (13)$$

in the case of ionic conduction processes as a function of the composition, are relatively lower at low PIL mole fraction ($E_a^* = 3.37 \text{ kJ}\cdot\text{mol}^{-1}$ at $x_{\text{PIL}} = 0.2$) than at high PIL mole fraction ($E_a^* = 5.29 \text{ kJ}\cdot\text{mol}^{-1}$ at $x_{\text{PIL}} = 0.8$). It should be important to notify also that the pseudo activation energy E_a^* of the ([Pyrr][NO₃] + PC) binary mixture increases monotonically as the function of the PIL composition in solution, without reaching any maximum value for any composition containing the PC, as shown in the figure S4 in the supporting information.

3.2.2. Viscosity measurements of the ([Pyrr][NO₃] + PC) binary mixture as a function of temperature and composition

Since ILs, both protic and aprotic, are more viscous than conventional solvents, in most applications, they can be used in mixtures with other less viscous compounds. Therefore, the viscosity of pure ILs and their mixtures with conventional solvents is an important property and their knowledge is primordial for each industrial processes [51]. The viscosity of the pure [Pyrr][NO₃] was firstly investigated from $T = (283.15 \text{ to } 353.15) \text{ K}$, and reported herein in the table 4 and shown in the figure 8. The viscosity of pure [Pyrr][NO₃] decreases with the

temperature from 58.9 mPa·s at $T = 283.15$ K to 9.28 mPa·s at $T = 353.15$ K. Furthermore, the effect of the presence of the PC on the viscosity of the solution was then examined as a function of the temperature from (283.15 to 353.15) K and over the whole composition range as reported in table 4 and shown in figures 8, and S5. Based on this information, it appears that the presence of PC decreases considerably the viscosity of the solution. For example at $T = 293.15$ K, we measured a viscosity close to (40.3, 13.1, and 5.8) mPa·s for binary mixture based on the PIL mole fraction, $x_{\text{PIL}} = 1.0, 0.5$ and 0.22 , respectively.

All experimental viscosity values were then adjusted by using the conventional VTF equation according to the following equation:

$$\eta = \eta_0 \exp\left(\frac{B_\eta}{T - T_0^\eta}\right) \quad (14)$$

where B_η , η_0 and T_0^η are adjustable parameters reported in table S11 of the supporting information along with their minimized standard deviation, as visualized in the figure 8.

The viscosity deviations from ideality $\Delta\eta$ were then calculated according to the following equation:

$$\Delta\eta = \eta - (x_{\text{PIL}} \eta_{\text{PIL}} + x_{\text{PC}} \eta_{\text{PC}}) \quad (15)$$

where x_{PIL} , x_{PC} , are the mole fractions of [Pyr][NO₃] and of PC. η , η_{PIL} , and η_{PC} , are the viscosity of the investigated mixtures, and those for the pure [Pyr][NO₃], and PC, respectively.

Figure 9 shows the viscosity deviations from the ideality as a function of the PIL mole fraction, x_{PIL} , and temperature for each binary mixture investigated. It can be seen in table 4 and from figure 9, that all $\Delta\eta$ values are negative at all temperatures studied, over the entire composition

range. Furthermore, $\Delta\eta$ values decrease by increasing the temperature. In fact, the temperature influences strongly these viscosity deviations, even if the observed composition at each maximum was found to be almost constant and independent of the temperature. It can be seen also that the absolute deviation values, $|\eta^E|$, are from (1 to 16) mPa·s from $T = (283.15$ to $353.15)$ K. Furthermore, the viscosity deviations show minima near to the median compositions range, which seem to be nearly shifted from $x_{\text{PIL}} = 0.4$ to $x_{\text{PIL}} = 0.6$ by increasing the temperature from (283.15 to 353.15) K, as already observed in the case of the excess molar volumes maxima.

According to Kauzmann and Eyring [52], the viscosity of a mixture depends strongly on its entropy, which is related to the liquid structure. Therefore, the viscosity deviation depends on molecular interactions as well as on the size and shape of the molecules. It can be seen in figure 9 that for all compositions and temperatures studied therein, the viscosity deviations are negative over the whole composition range. This behaviour is characteristic of mixtures without strong specific interactions, a *contrario*, of [Pyrr][NO₃] aqueous solutions,[43] which exhibit positive deviations. This difference between PC and water solutions containing the [Pyrr][NO₃] could be attributed to the break-up of the self-association through hydrogen bonding.

On the basis of the theory of absolute reaction rates [53,54], the excess Gibbs energy (ΔG^{E*}) of activation of viscous flow were calculated by using the following equation:

$$\frac{\Delta G^{E*}}{RT} = \left[\ln \left(\frac{\eta V_m}{\eta_2 V_{m,2}} \right) - x_1 \ln \left(\frac{\eta_1 V_{m,1}}{\eta_2 V_{m,2}} \right) \right] \quad (16)$$

where V_m , $V_{m,1}$, and $V_{m,2}$ are the molar volumes of the binary mixture and of the pure components 1 and 2, respectively. Calculated values of ΔG^{E*} are tabulated in table S12 in the supporting information. The observed values of ΔG^{E*} for the binary mixture are positive as shown in figure 10 and ΔG^{E*} values steadily increases with the PIL mole fraction up to a concentration close to $x_{PIL} = 0.4$. In the case of the ([Pyrr][NO₃] + PC) binary mixture, the observed ΔG^{E*} values are positive for the entire mole fraction. Positive values indicate the specific interaction leading to complex formation through intermolecular hydrogen bonding interaction between unlike molecules compared to like molecules [55,56]. This observation is also compatible with the decrease of these specific interaction between PC and PIL (especially the cation) as ΔG^{E*} values decrease, as the H-bonds break-up, with temperature.

3.2.3. Walden rule and ionicity

Classical Walden rule diagram was used to determine the ionicity of studied ionic liquids. The ionic mobility is represented through the equivalent conductivity, $\Lambda = V_m \cdot \sigma$ (S·cm²·mol⁻¹), as a function of fluidity, $\phi = 1/\eta$ (Poise⁻¹), of the medium, which is related to the mobility of the ions [57]. Figure 11 shows the variation of $\log(\Lambda)$ versus $\log(1/\eta)$ at various temperatures from at temperatures from 298.15 K to 353.15 K and composition for selected (PIL + PC) solutions. The ideal line obtained for ionic mobility is established by using aqueous KCl solutions at high dilution [58]. The ionicity rule of the PIL solutions studied are presented and then compared with zones corresponding to individual types of electrolytes, as shown in figure 11, as “good”, “poor” and “superionic” ionic liquids, respectively. All compositions studied in this work are conforming to the Walden rule. Furthermore, the ionicity of the pure [Pyrr][NO₃] PIL studied seems to be regrouped in a wide zone on the Walden plot, which corresponds to the “good” ionic

liquids zone of this representation. From this figure, it appears also that the presence of PC affects strongly the Walden plot of the [Pyrr][NO₃] solutions involved since the ionicity of these mixtures changes from “good” to “poor” electrolytes by increasing the PC concentration in the PIL solution. The curve for pure PIL appears above the ideal line, suggesting a super-ionic behaviour that could result from proton hopping *vs* simple vehicular mechanism. The super-ionic behaviour of [Pyrr][NO₃] *via* a vehicle mechanism has already been shown in a previous work.[45] As already mentioned by Greaves *et al.* [59], due to the hydrate structure of the [NO₃]⁻ anion, which reduces the jump of protons in solution, this super-ionic character is maintained, herein, despite the high residual water (2000x10⁻⁶) in the [Pyrr][NO₃] PIL. Our group has also previously reported in the case of the pyrrolidinium hydrogen sulfate (a super-ionic PIL) by using a pulse gradient NMR analysis, that the Grotthuss mechanism is observed in (PIL + water) mixture containing more than 8 wt % of water in solution [60]. In the case of ([Pyrr][NO₃] + PC) binary mixture, the increase of PC concentration in solution reduces significantly the viscosity, but also the equivalent conductivity and thus the ionic mobility of the mixture. In other words, due to the strong interaction between PC and ions in solution, the addition of PC in the [Pyrr][NO₃] PIL has a negative impact on the ionicity of the solution. This behaviour can be also explained by the fact that the pure PIL has higher values of conductivity and molar volume than its solutions with PC.

4. Conclusions

The viscosity, density and conductivity of the ([Pyrr][NO₃] + PC) binary mixture as a function of composition and of temperature from (283.15 to 333.15) K were determined. From these experimental results, deviations from ideality and excess properties were then deduced. This investigation shows negative deviations from the ideal behaviour for all properties covered in

this work independently of the temperature and composition studied. Excess properties of ([Pyrr][NO₃] + PC) system were then calculated at each temperature and fitted according to the Redlich–Kister polynomial type fitting equation. The ionicity of each solution was evaluated according to the Walden rule by using the molar conductivity and fluidity properties as a function of the temperature. From experimental values, apparent molar volumes, thermal expansion coefficients α_p , and excess Gibbs energies (ΔG^{E*}) of activation of viscous flow were then calculated for this involved binary system. All reported thermodynamic and transport properties of the ([Pyrr][NO₃] + PC) binary mixture were then analysed in terms of the structure and interactions changes in solution. Finally, reported data were compared to those published by our group previously in the case of the ([Pyrr][NO₃] + water) solution. This comparison provides useful information concerning the role of H-bonds in solution for mixture containing an PIL mixed with a polar and associative (water) or with a polar and non-associative (PC) solvent.

Acknowledgement

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Supplementary data

Additional Supporting Information includes experimental conductivities, calculated entropy and volumetric properties of the ([Pyrr][NO₃] + PC) binary mixture as a function of composition and temperature, as well as fitting parameters obtained with the correlation of experimental data with the Redlich–Kister, Arrhenius and VTF type fitting equations. This material is available free of charge via the Internet at <http://www.sciencedirect.com>.

Figure 1. Density measurements, ρ , of the ([Pyrr][NO₃] + PC) binary mixture as a function of the [Pyrr][NO₃] mole fraction composition, x_{PIL} , at: \circ , $T = 283.15$ K; \bullet , 293.15 K; \square , 303.15 K; \blacksquare , 313.15 K; ∇ , 323.15 K; \blacktriangledown , 333.15 K; \triangle , 343.15 K; \blacktriangle , 353.15 K. The lines represent cubic polynomial-type fittings with the parameters indicated in the table S1 providing on the supporting information.

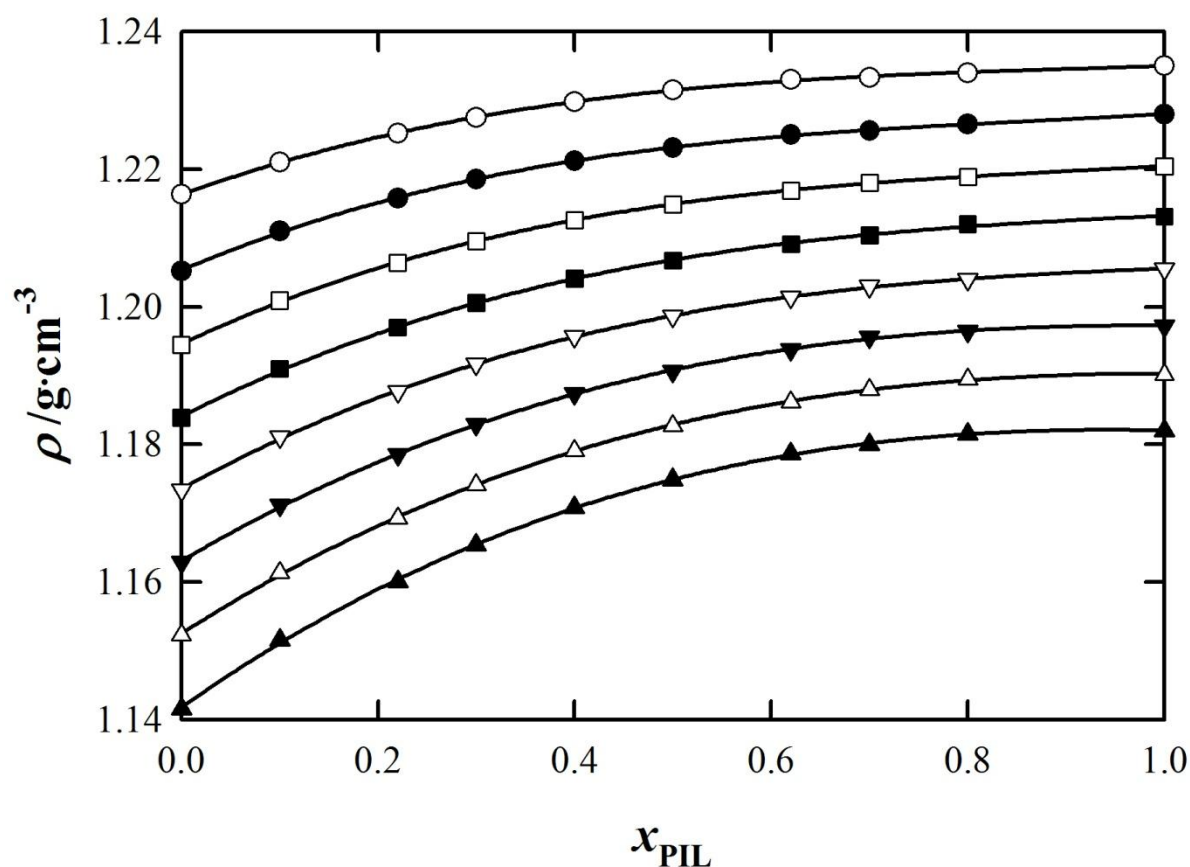


Figure 2. Excess molar volumes for ([Pyrr][NO₃] + PC) binary mixture as a function of the [Pyrr][NO₃] mole fraction composition, x_{PIL} , at: \circ , $T = 283.15$ K; \bullet , 293.15 K; \square , 303.15 K; \blacksquare , 313.15 K; ∇ , 323.15 K; \blacktriangledown , 333.15 K; \triangle , 343.15 K; \blacktriangle , 353.15 K. The lines represent the Redlich-Kister-type fittings with the parameters indicated in the table S13 of the supporting information.

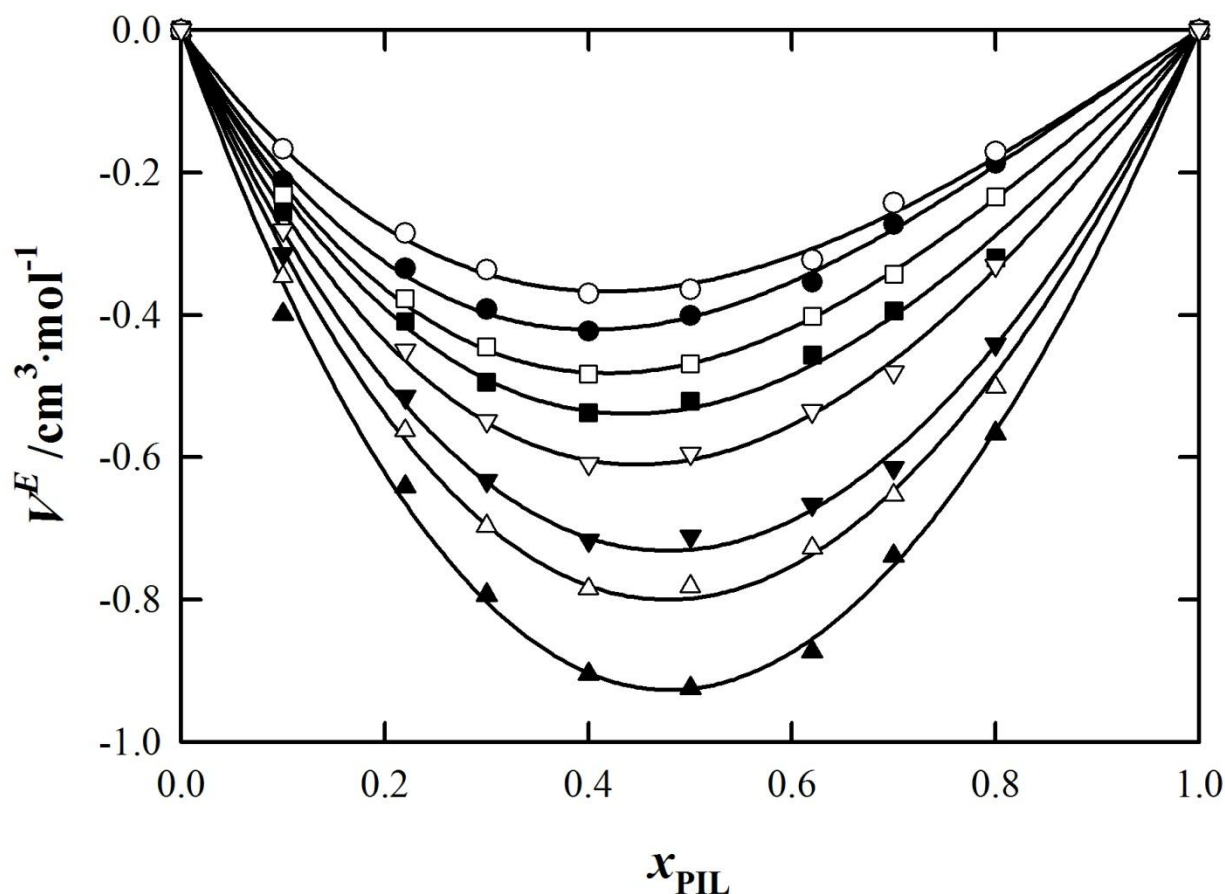


Figure 3. Apparent molar volumes: a) $V_{\phi, \text{PIL}}$ and b) $V_{\phi, \text{PC}}$ for ([Pyrr][NO₃] + PC) binary mixture as a function of the [Pyrr][NO₃] mole fraction composition, x_{PIL} , at: \circ , $T = 283.15$ K; \bullet , 293.15 K; \square , 303.15 K; \blacksquare , 313.15 K; ∇ , 323.15 K; \blacktriangledown , 333.15 K; \triangle , 343.15 K; \blacktriangle , 353.15 K.

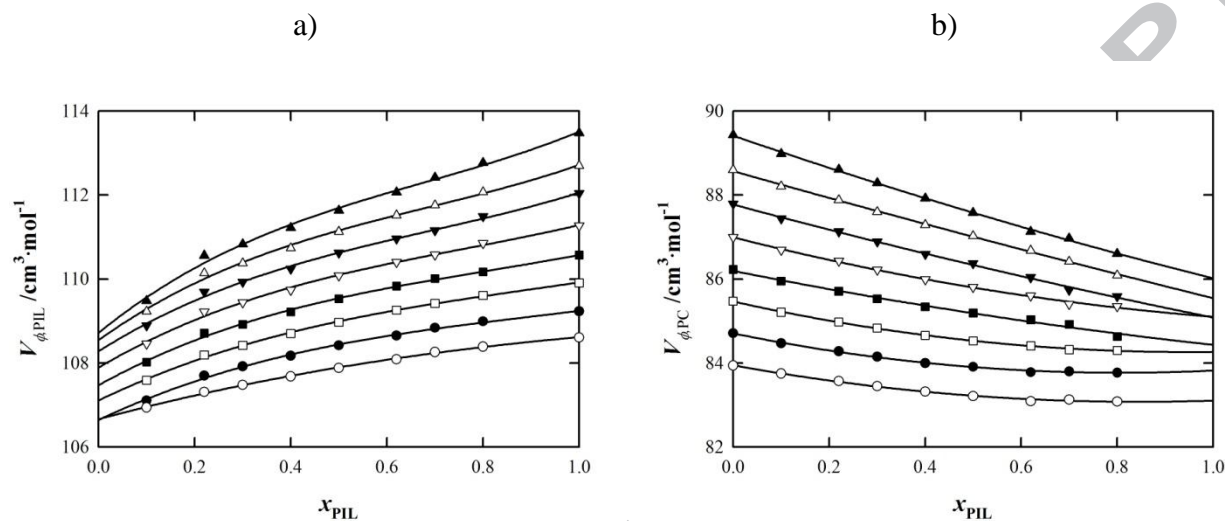


Figure 4. Partial molar volumes: a) $\bar{V}_{m, \text{PIL}}$ and b) $\bar{V}_{m, \text{PC}}$ for ([Pyr][NO₃] + PC) binary mixture as a function of the [Pyr][NO₃] mole fraction composition, x_{PIL} , at: \circ , $T = 283.15$ K; \bullet , 293.15 K; \square , 303.15 K; \blacksquare , 313.15 K; ∇ , 323.15 K; \blacktriangledown , 333.15 K; \triangle , 343.15 K; \blacktriangle , 353.15 K and 0.1 MPa.

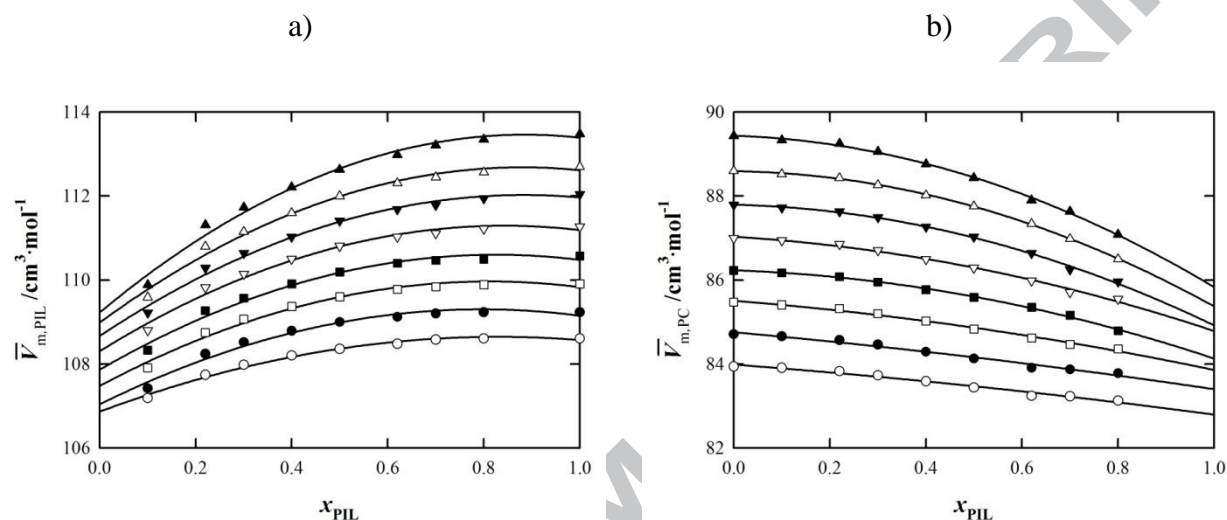


Figure 5. Excess thermal expansion coefficient of the ([Pyrr][NO₃] + PC) binary mixture as a function of the [Pyrr][NO₃] volume fraction, ϕ_{PIL} at: \circ , $T = 283.15$ K; \bullet , 293.15 K; \square , 303.15 K; \blacksquare , 313.15 K; ∇ , 323.15 K; \blacktriangledown , 333.15 K; \triangle , 343.15 K; \blacktriangle , 353.15 K and 0.1 MPa. The lines represent the Redlich-Kister-type fittings with the parameters indicated in the table S13 of the supporting information.

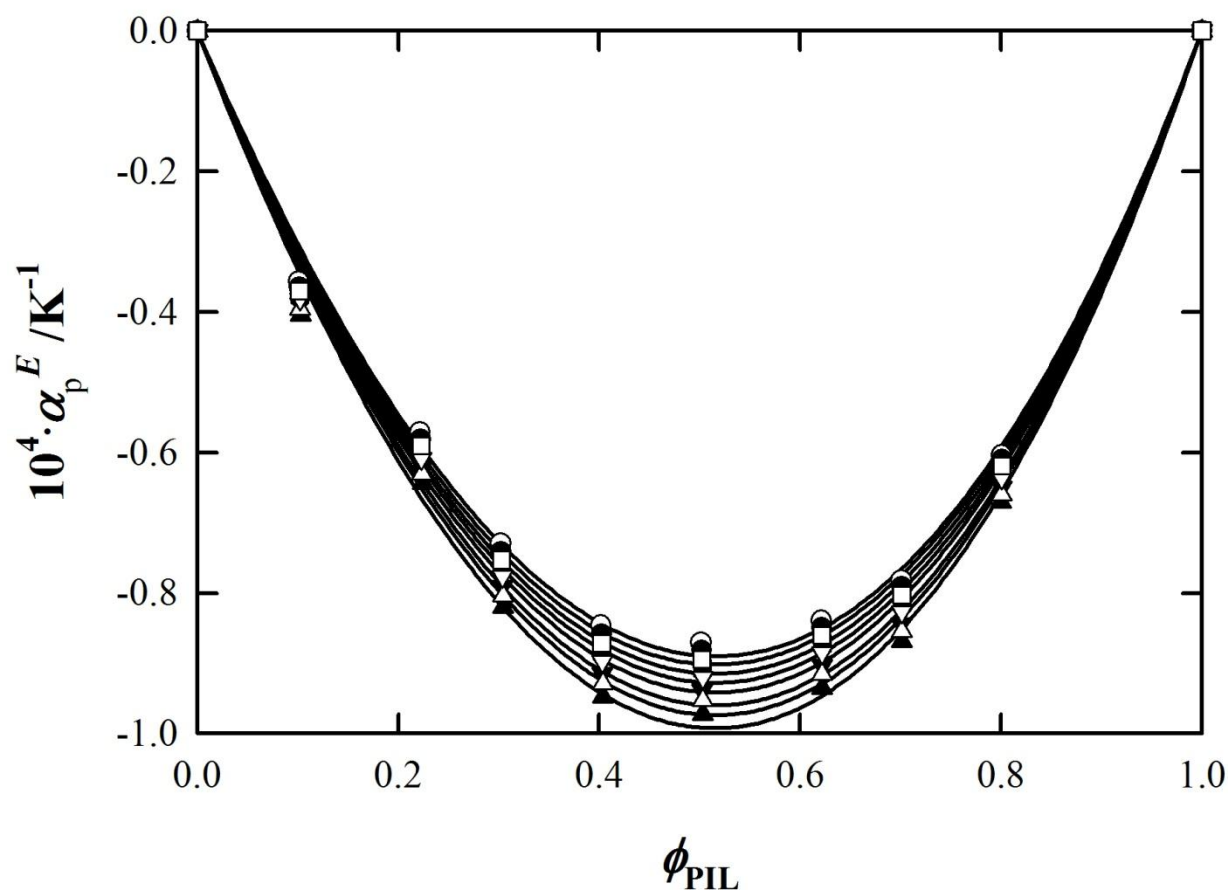


Figure 6. Conductivity measurements, σ , of the ([Pyr][NO₃] + PC) binary mixture as a function of the temperature and 0.1 MPa at $x_{\text{PIL}} =$: ●, 0.10; □, 0.22; ■, 0.30; ▼, 0.50; ◇, 0.80; ◆, 1. The lines represent the VTF type fitting of the experimental data with parameters reported in table S8 of the supporting information. The insert plot shows the sharp drop in conductivity at temperatures below 298.15 K observed in the case of $x_{\text{PIL}} = 0.80$.

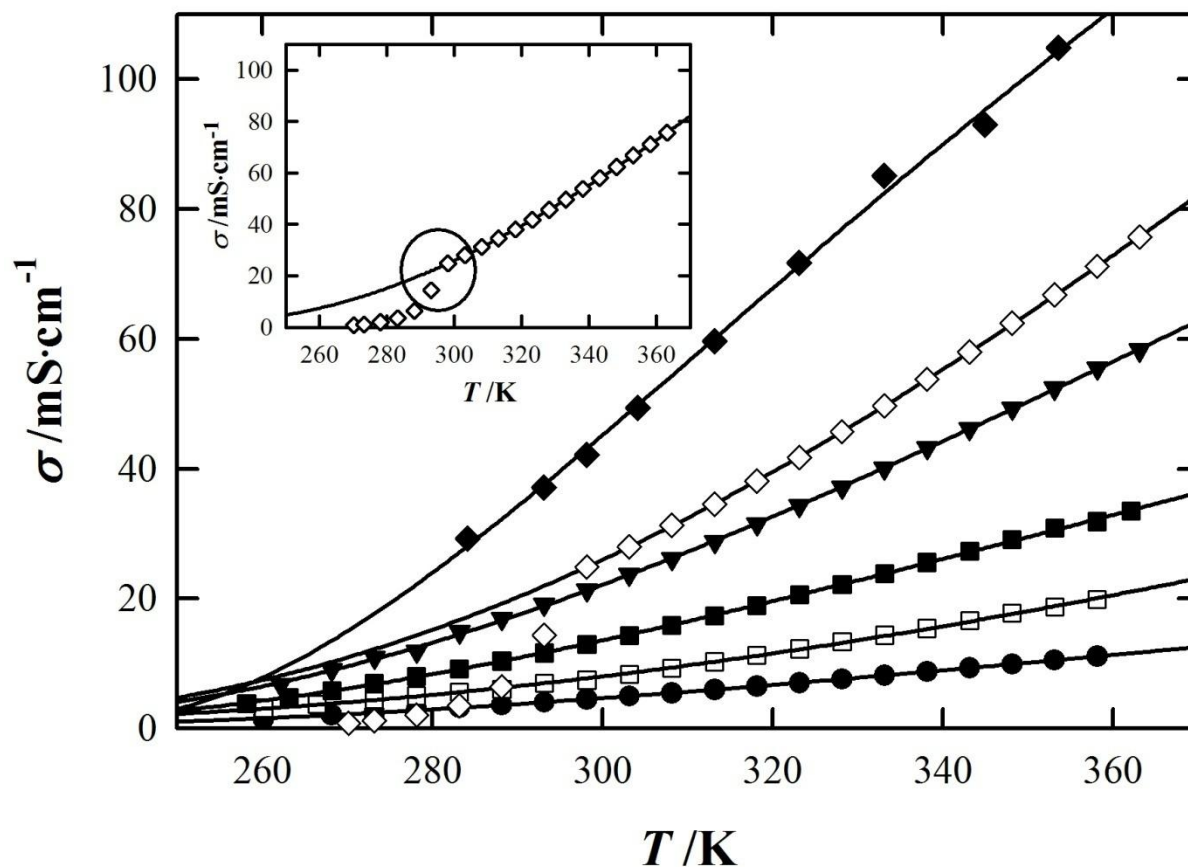


Figure 7. Conductivity measurements, σ , of the ([Pyrr][NO₃] + PC) binary mixture as a function of the [Pyrr][NO₃] weight fraction composition, w_{PIL} , at \diamond , $T = 298.15$ K (data are provided in the table S9 in the supporting information) and 0.1 MPa. The insert plot provides the conductivity measurements, σ , of the ([Pyrr][NO₃] + PC) binary mixture as a function of the [Pyrr][NO₃] mole fraction, x_{PIL} at: \blacklozenge , $T = 273.15$ K; \circ , 283.15 K; \bullet , 293.15 K; \square , 303.15 K; \blacksquare , 313.15 K; ∇ , 323.15 K; \blacktriangledown , 333.15 K; \triangle , 343.15 K; \blacktriangle , 353.15 K and 0.1 MPa.

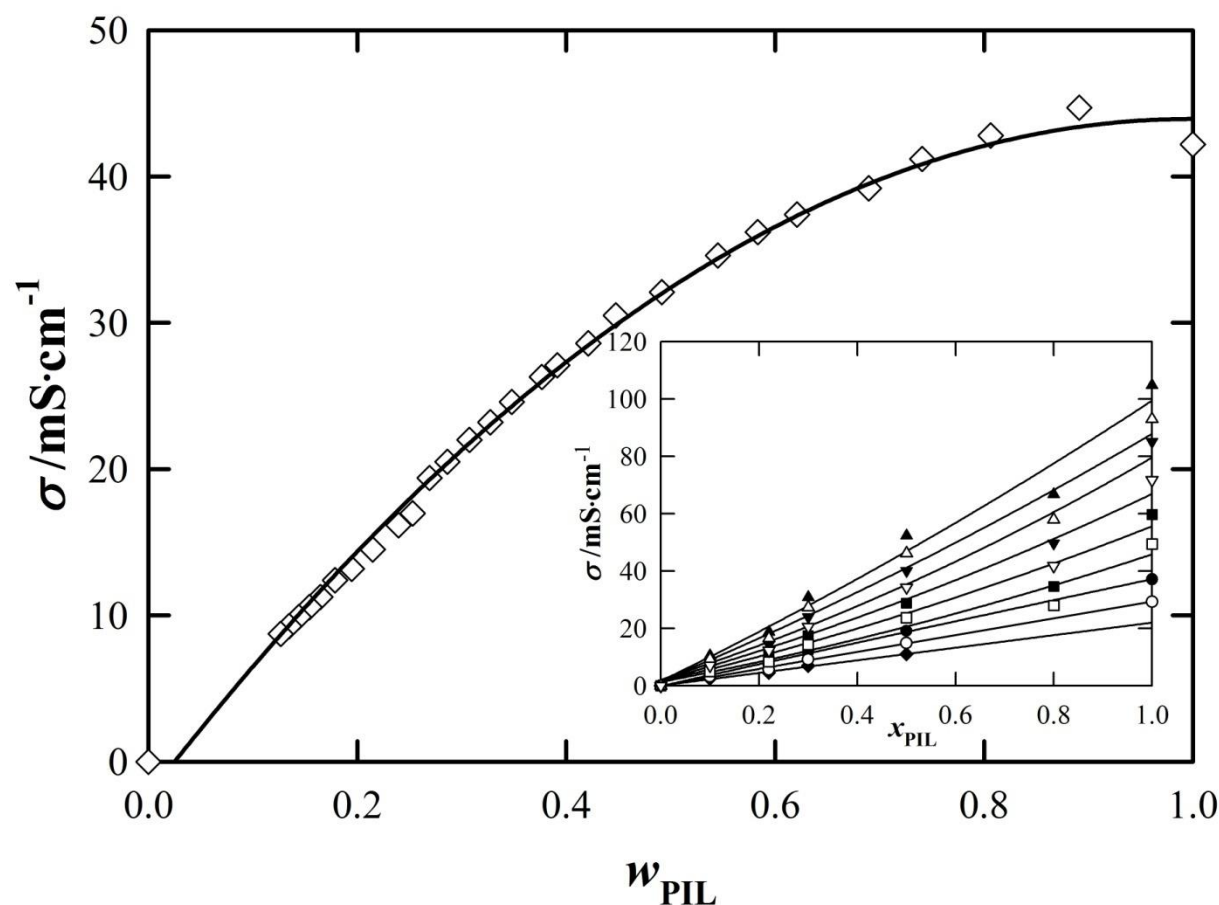


Figure 8. Viscosity measurements, η , of the ([Pyrr][NO₃] + PC) binary mixture as a function of the temperature from (283.15 to 353.15) K and 0.1 MPa at $x_{\text{PIL}} =$: \circ , 0; \bullet , 0.10; \square , 0.22; \blacksquare , 0.30; ∇ , 0.40; \blacktriangledown , 0.50; \triangle , 0.62; \blacktriangle , 0.70; \diamond , 0.80; \blacklozenge , 1. The lines represent the VTF type fitting of the experimental data with parameters reported in table S11 of the supporting information.

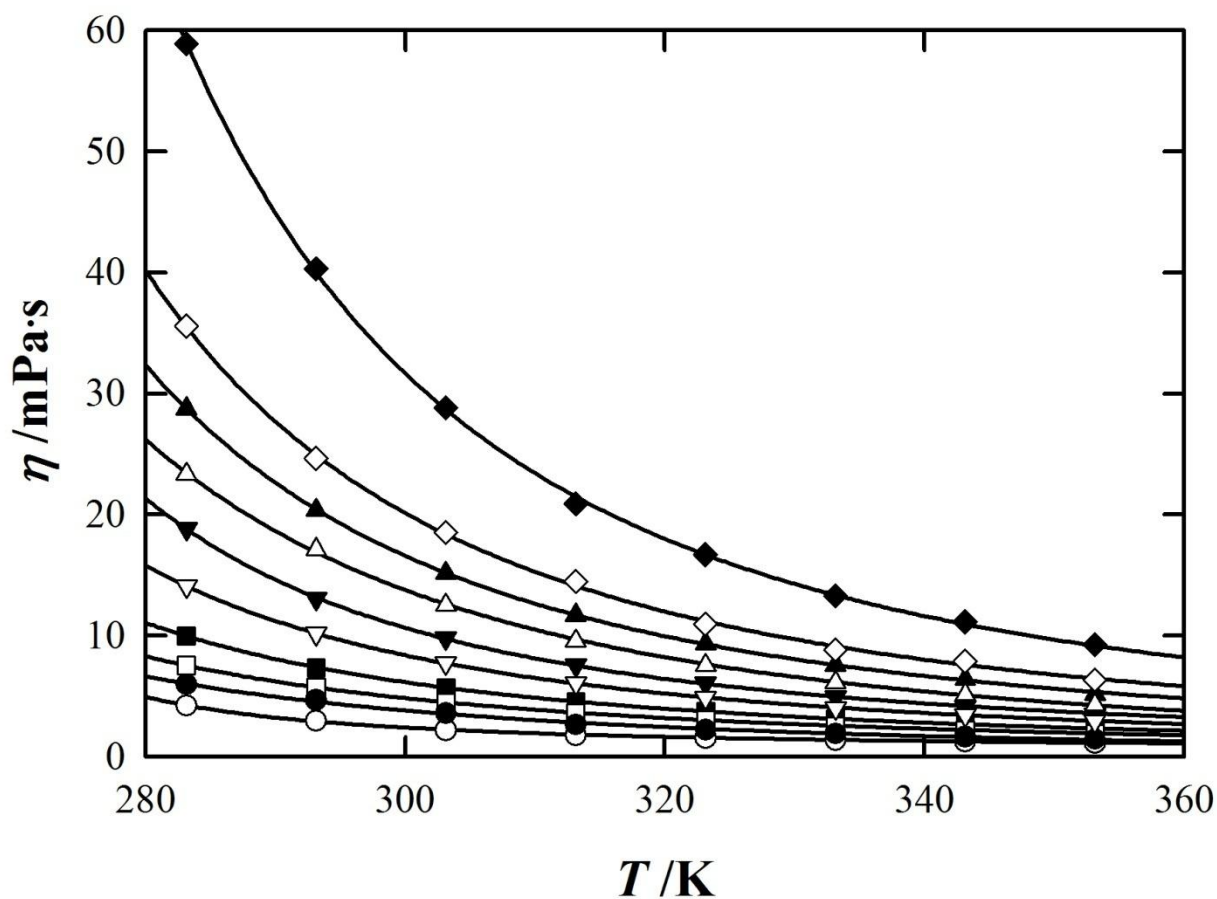


Figure 9. Viscosity deviations from the ideality of the ([Pyrr][NO₃] + PC) binary mixture as a function of the [Pyrr][NO₃] mole fraction composition, x_{PIL} , at: \circ , $T = 283.15$ K; \bullet , 293.15 K; \square , 303.15 K; \blacksquare , 313.15 K; ∇ , 323.15 K; \blacktriangledown , 333.15 K; \triangle , 343.15 K; \blacktriangle , 353.15 K at 0.1 MPa. The lines represent the Redlich-Kister-type fittings with the parameters indicated in the Table S13 of the supporting information.

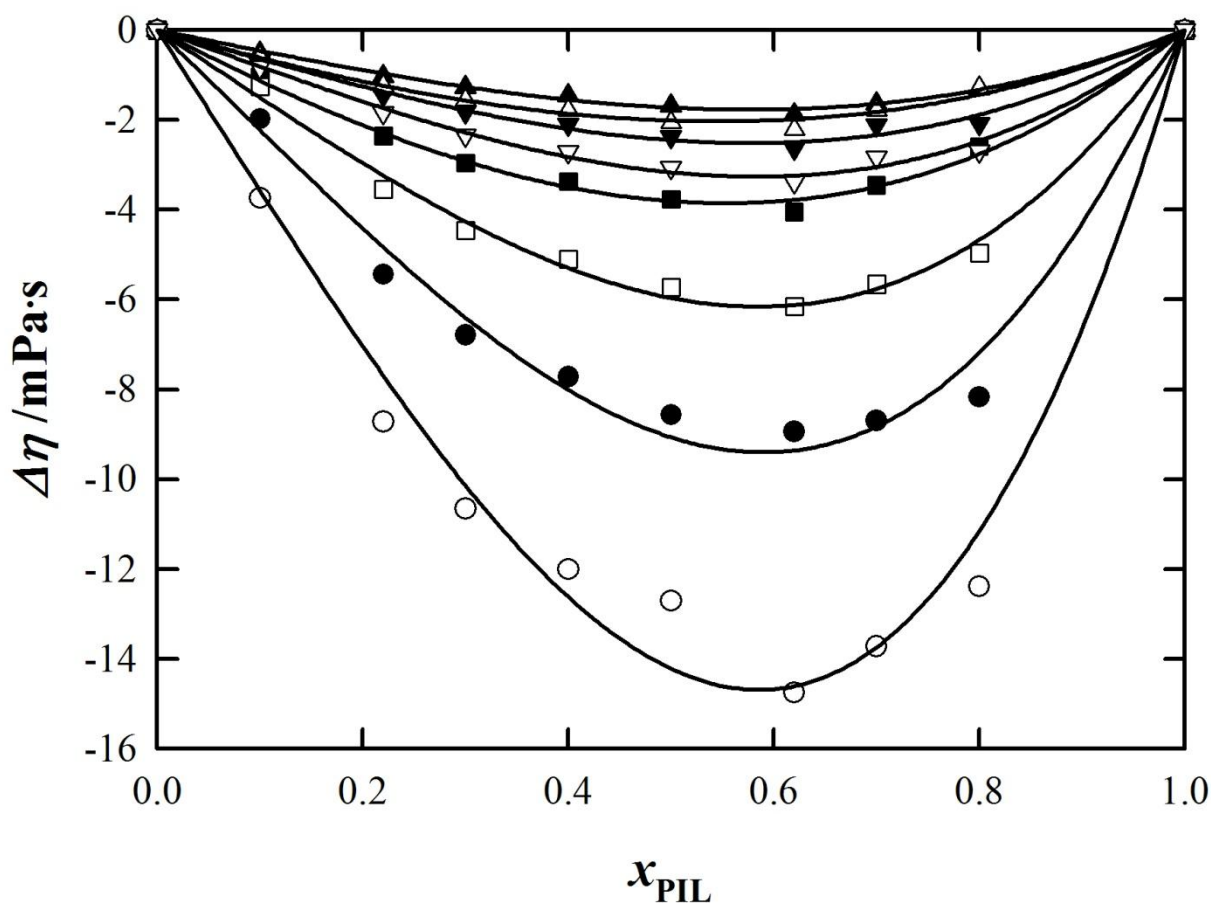


Figure 10. Comparison of the excess Gibbs energy of activation of viscous flow, ΔG^{E*} for binary mixtures of ([Pyrr][NO₃] + PC) as a function of PIL mole fraction composition, x_{PIL} , at: \square and solid line, $T = 303.15$ K; ∇ and dashed line, 323.15 K; \blacktriangle and dotted line, 353.15 K at 0.1 MPa. The lines represent the Redlich-Kister-type fittings.

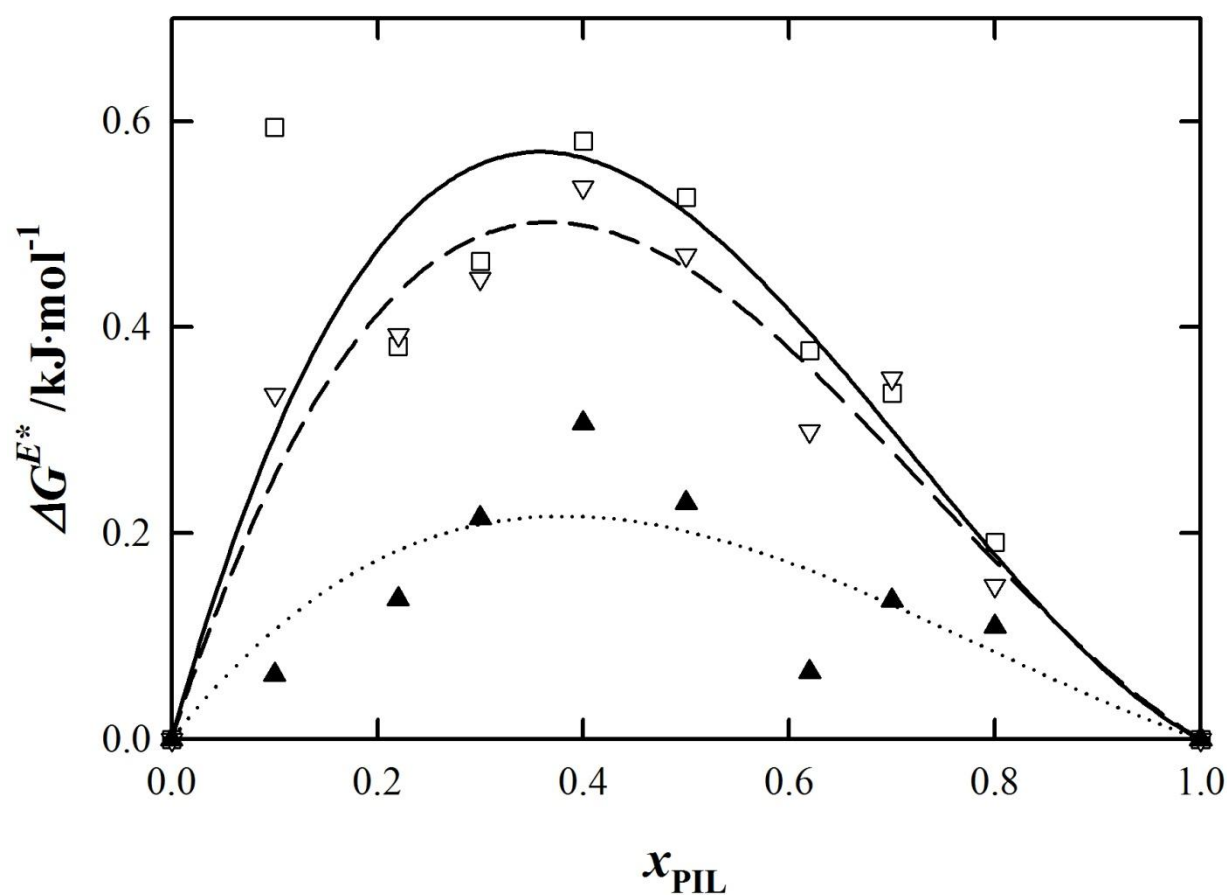


Figure 11. Walden plot of the ([Pyrr][NO₃] + PC) binary mixture as a function of the temperature from (283.15 to 353.15) K and 0.1 MPa at x_{PIL} =: ●, 0.10; □, 0.22; ■, 0.30; ▼, 0.50; ◇, 0.80; ◆, 1.

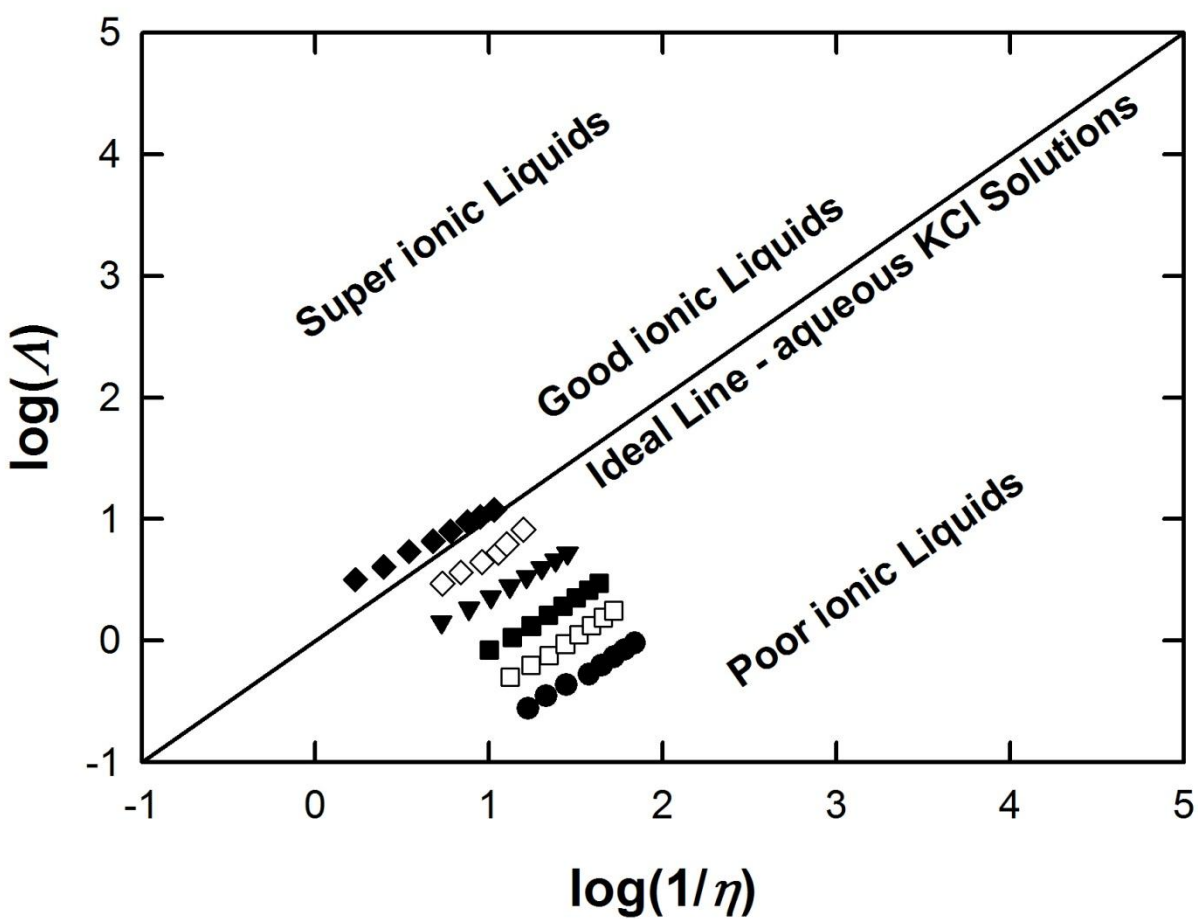


Table 1. Source, abbreviation, purity, and water content for each chemical sample reported during this work.

Chemical name	Source	Abbreviation	Mole fraction	Water content
			Purity	10^{-6}
propylene carbonate	Fluka	PC	0.9999	$< 10^b$
pyrrolidine		-	0.99	-
1,2-dichloroethane		DCE	0.99	-
nitric acid solution, 68 % in water		HNO ₃	-	-
Dried Pyrrolidinium nitrate (solid state) at 298 K	synthesized in-house	[Pyrr][NO ₃]	$> 0.98^a$	$< 100^b$
Pyrrolidinium nitrate (liquid state) at $T = 298$ K		[Pyrr][NO ₃]	$> 0.98^a$	$2000^{b,c}$

^a Determined by NMR analysis; ^b precision and accuracy of the reported experimental data are close to (5 and 10) %, respectively; ^c This purity state was defined into this paper as the pure PIL.

Table 2. Density, ρ , measurements and excess molar volumes, V^E of ([Pyrr][NO₃] + PC) binary mixture as a function of [Pyrr][NO₃] mole fraction composition, x_{PIL} , for a temperature range from (283.15 to 353.15) K at 0.1 MPa.

T/K	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15
x_{PIL}	$\rho/\text{g}\cdot\text{cm}^{-3}$ ^a							
0	1.2163	1.2052	1.1945	1.1839	1.1734	1.1629	1.1523	1.1416
0.10	1.2210	1.2110	1.2009	1.1910	1.1811	1.1712	1.1614	1.1516
0.22	1.2252	1.2158	1.2064	1.1970	1.1877	1.1785	1.1693	1.1601
0.30	1.2275	1.2185	1.2095	1.2006	1.1917	1.1829	1.1742	1.1654
0.40	1.2298	1.2212	1.2126	1.2041	1.1957	1.1874	1.1791	1.1708
0.50	1.2315	1.2231	1.2149	1.2067	1.1986	1.1906	1.1827	1.1749
0.62	1.2330	1.2250	1.2169	1.2091	1.2014	1.1938	1.1862	1.1787
0.70	1.2333	1.2256	1.2180	1.2104	1.2030	1.1956	1.1880	1.1800
0.80	1.2340	1.2265	1.2189	1.2120	1.2040	1.1965	1.1895	1.1815
1	1.2350	1.2280	1.2204	1.2131	1.2055	1.1972	1.1902	1.1820
	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$ ^b							
0	0	0	0	0	0	0	0	0
0.10	-0.167	-0.212	-0.231	-0.255	-0.281	-0.314	-0.346	-0.399
0.22	-0.285	-0.335	-0.377	-0.409	-0.450	-0.515	-0.562	-0.641
0.30	-0.337	-0.392	-0.445	-0.494	-0.549	-0.633	-0.696	-0.793
0.40	-0.370	-0.423	-0.483	-0.537	-0.609	-0.717	-0.784	-0.904
0.50	-0.364	-0.401	-0.469	-0.521	-0.594	-0.711	-0.781	-0.924
0.62	-0.323	-0.354	-0.402	-0.456	-0.535	-0.666	-0.727	-0.873
0.70	-0.243	-0.273	-0.343	-0.394	-0.480	-0.615	-0.653	-0.738
0.80	-0.171	-0.187	-0.234	-0.320	-0.331	-0.441	-0.501	-0.566
1	0	0	0	0	0	0	0	0

^a precision and accuracy of the reported experimental data are close to $\pm 5\times 10^{-5}$ $\text{g}\cdot\text{cm}^{-3}$ and 0.1 %, respectively. ^b precision and accuracy of the reported calculated data are close to $\pm 7\times 10^{-3}$ $\text{cm}^3\cdot\text{mol}^{-1}$ and 0.5 %, respectively.

Table 3. Partial molar volumes at infinite dilution, for [Pyrr][NO₃], $\bar{V}_{m,\text{PIL}}^\infty$, and for PC, $\bar{V}_{m,\text{PC}}^\infty$, and molar volumes $V_{m,i}$ of the pure liquids as a function of temperature from (283.15 to 353.15) K at 0.1 MPa.

T/K	$\bar{V}_{m,\text{PIL}}^\infty / \text{cm}^3 \cdot \text{mol}^{-1}$	$V_{m,\text{PIL}} / \text{cm}^3 \cdot \text{mol}^{-1} \text{ }^a$	$\bar{V}_{m,\text{PC}}^\infty / \text{cm}^3 \cdot \text{mol}^{-1}$	$V_{m,\text{PC}} / \text{cm}^3 \cdot \text{mol}^{-1} \text{ }^a$
283.15	106.87	108.607	82.80	83.936
293.15	107.04	109.226	83.40	84.708
303.15	107.48	109.907	83.86	85.467
313.15	107.86	110.568	84.13	86.232
323.15	108.30	111.265	84.79	87.004
333.15	108.67	112.036	84.92	87.789
343.15	108.98	112.695	85.37	88.597
353.15	109.22	113.477	85.83	89.427

^a Precision and accuracy of the reported calculated data are close to $\pm 3 \times 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1}$ and 0.2 %, respectively.

Table 4. Viscosity, η , measurements and viscosity deviations from the ideality, $\Delta\eta$ of ([Pyrr][NO₃] + PC) binary mixture as a function of [Pyrr][NO₃] mole fraction composition, x_{PIL} , for a temperature range from (283.15 to 353.15) K at 0.1 MPa.

x_{PIL}	T/K							
	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15
$\eta/\text{mPa}\cdot\text{s}^{\text{a}}$								
0	4.25	2.96	2.20	1.80	1.56	1.40	1.26	1.15
0.10	5.97	4.71	3.60	2.66	2.24	1.91	1.65	1.45
0.22	7.55	5.73	4.50	3.64	3.04	2.57	2.20	1.91
0.30	9.98	7.37	5.71	4.57	3.75	3.14	2.68	2.32
0.40	14.10	10.17	7.73	6.07	4.91	4.06	3.44	2.95
0.50	18.85	13.06	9.78	7.59	6.07	4.97	4.16	3.54
0.62	23.36	17.16	12.55	9.60	7.57	6.15	5.19	4.30
0.70	28.76	20.39	15.17	11.72	9.33	7.61	6.42	5.20
0.80	35.56	24.65	18.53	14.49	10.97	8.83	7.91	6.35
1	58.87	40.29	28.81	20.91	16.70	13.30	11.17	9.28
$\Delta\eta/\text{mPa}\cdot\text{s}^{\text{b}}$								
0	0	0	0	0	0	0	0	0
0.10	-3.74	-1.98	-1.26	-1.05	-0.83	-0.68	-0.60	-0.51
0.22	-8.72	-5.44	-3.55	-2.36	-1.85	-1.45	-1.24	-1.03
0.30	-10.66	-6.79	-4.47	-2.96	-2.35	-1.83	-1.55	-1.27
0.40	-12.00	-7.72	-5.11	-3.37	-2.71	-2.10	-1.78	-1.45
0.50	-12.71	-8.57	-5.73	-3.77	-3.06	-2.38	-2.06	-1.68
0.62	-14.75	-8.94	-6.15	-4.05	-3.38	-2.63	-2.21	-1.89
0.70	-13.72	-8.70	-5.66	-3.46	-2.83	-2.12	-1.78	-1.64
0.80	-12.39	-8.17	-4.96	-2.60	-2.70	-2.09	-1.28	-1.30
1	0	0	0	0	0	0	0	0

^a precision and accuracy of the reported experimental data are close to (1 and 3) %, respectively.

^b precision and accuracy of the reported calculated data are expected to be close to (2 and 5) %, respectively.

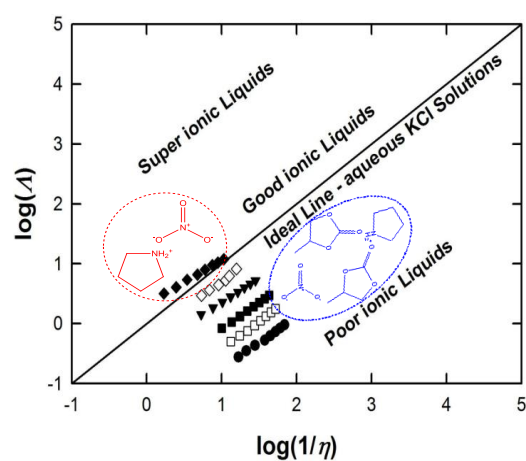
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Highlights

- ρ , η , and σ were measured for ([Pyrr][NO₃] + PC) systems.
- Excess molar properties were deduced from the experiments.
- Ionicity of mixtures was evaluated by Walden rule as function of T and C.
- Results were discussed in terms of molecular interactions and structures.